Studies on the Determination of Metals by Extraction Method of Metal Organic Compounds. VIII : Determination of Iron with Antipyrine

Studies on the Determination of Metals by Extraction Method of Metal Organic Compounds. VIII
Determination of Iron with Antipyrine*

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Synopsis

Iron forms a red compound with antipyrine and potassium thiocyanate, and this compound can be extracted with an organic solvent and the extract obtained shows a special light absorbance. Its absorbance was measured by the Beckman model DU spectrophotometer and the microdetermination of iron was performed. Ethyl acetate was the best extraction solvent and a small amount of iron below 1 γ could be determined at the optimum wave length of 470 mμ.

I. Introduction

The present author has previously reported the determination of cobalt[1], mercury and bismuth[2] using antipyrine and ammonium thiocyanate, and the method is also applicable to the case of iron. There are numerous reports on the microdetermination of iron by the extraction of iron thiocyanate with organic solvents[3]. In most cases, the extraction was made with isobutyl alcohol. When antipyrine is used, extraction with ethyl acetate gives a large molecular extinction coefficient, which seems to make it possible to determine a minute amount of iron by the extraction of iron thiocyanate. A brief report of the results will be given below.

II. Experimental results

1. Apparatus and reagents

The extinctance was measured with the Beckman model DU spectrophotometer using 1 cm cell and the reagents were as follows: Standard iron solution (10 γ/ml) prepared from electrolytic iron; antipyrine solution (5 per cent solution of antipyrine JP); potassium thiocyanate solution (20 per cent aqueous solution of the guaranteed grade potassium thiocyanate); sulfuric and nitric acids (the guaranteed grade); hydrochloric acid (redistilled before use); as the organic solvents, benzene,

* The 802nd report of the Research Institute for Iron, Steel and other Metals. Published in the Journal of the Chemical Society of Japan, **75** (1954), 968.

(1) E. Sudô, J. Chem. Soc. Japan, **74** (1953), 658; Sci. Rep. RITU, **A6**, (1954), 324.
(2) E. Sudô, J. Chem. Soc. Japan, **74** (1953), 918; Sci. Rep. RITU, **A7** (1955), .
(3) J. B. Thompson, Ind. Eng. Chem., Anal. Ed., **16** (1944), 646; H. S. Frank and R. L. Oswalt, J. Am. Chem. Soc., **69** (1947), 1321; J. T. Woads and M. G. Mellon, Ind. Eng. Chem., Anal. Ed., **13** (1941), 551; C. A. Peters and C. L. French, ibid., **13** (1941), 604; H. N. Stokes and J. R. Cain, J. Amer. Chem. Soc., **29** (1907), 409; A. Anales, soc. quim. argentina, **29** (1941), 48.

toluene, xylene, ethyl acetate, amyl acetate, butyl acetate, amyl alcohol, butyl alcohol, carbon tetrachloride, and chloroform; all were of the first grade reagents.

2. Experimental porcedures

The iron solution was placed in a separatory funnel, and to it 5 ml of 0.1N hydrochloric acid, 5 ml of 20 per cent potassium thiocyanate solution, and 5 ml of 5 per cent antipyrine solution were added, and the mixture was shaken with 5 ml of ethyl acetate. After allowing the two layers to separate, the organic solvent layer was transferred to the 1 cm cell and its absorbance was measured.

3. Absorbance curve

Absorbance curve was obtained by measuring the light transmittance of the extract at 320~1000 mμ wave length. Fig. 1 shows the absorbance curves obtained by using ethyl acetate as the standard. Curve A is the absorbance of the blank test and curve B is that for 5 γ of iron. As seen from this figure, there was an absorbance at around 470 mμ, and the absorbance of the blank test became greater in the ultraviolet region below 320 mμ. Therefore, the subsequent measurement was made at 470 mμ and, as shown in the later experiments, it was found that the absorbance of extract obeyed to Beer's law.

Fig. 2 shows the absorbance curve obtained by using the extract of the blank test as the standard. Curve A is the absorbance of the case containing 2 γ of iron, curve B that for 5 γ of iron, and curve C that for 10 γ of iron.

4. Solvent

Absorbances of the extracts with various solvents were compared with one another and the absorbance

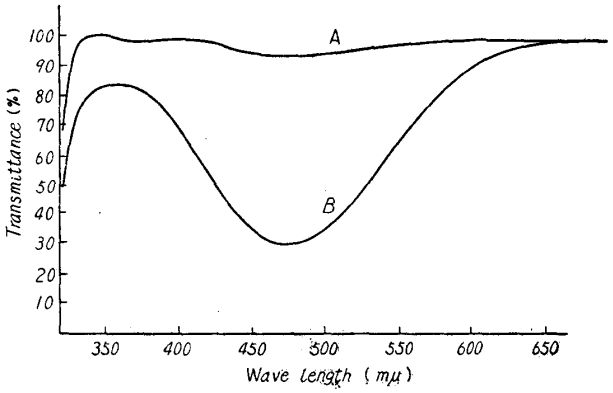

Fig. 1. Transmittance curve of iron-antipyrine-thiocyanate complex in ethyl acetate.
A: Blank test (ethyl acetate as standard)
B: Iron 5 γ (ethyl acetate as standard)

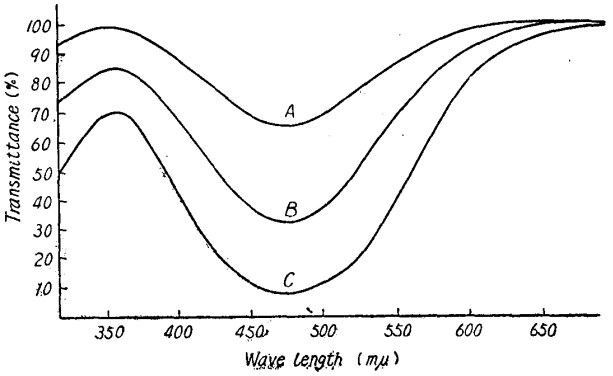

Fig. 2. Transmittance curve of iron-antipyrine-thiocyanate complex in ethyl acetate.
A: Iron 2 γ (blank test as standard)
B: Iron 5 γ (blank test as standard)
C: Iron 10 γ (blank test as standard)

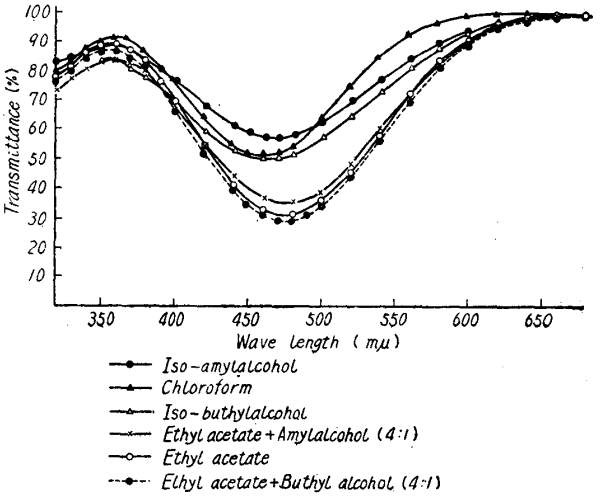

Fig. 3. Transmittance curve of iron-antipyrine-thiocyanate complex in various solvents.

curves are shown in Fig. 3. In these cases, the amount of iron was 5 γ and the extraction was made with 5 ml of each solvent. Molecular extinction coefficient of each solvent against 1 mole of iron at 470 mμ is shown in Table 1, from which it can be seen that isoamyl alcohol shows the smallest value. Isobutyl alcohol, often used for the extraction of iron thiocyanate, has the smaller extinction coefficient than ethyl acetate, while a mixed solvent of ethyl acetate and butyl alcohol (4 : 1) has somewhat larger coefficient than ethyl acetate alone. Amyl and butyl acetate have larger coefficient than isoamyl alcohol. The optimum absorption of chloroform shifts about 10 mμ towards a shorter wave length and its molecular extinction coefficient at 480 mμ is the same as that of isobutyl alcohol. The subsequent extractions were therefore carried out with ethyl acetate. Three extractions respectively with 5 ml of ethyl acetate gave the results shown in Table 2, which indicates that the extraction is almost complete at the first extraction. Extraction was not effected by carbon tetracholride, benzene, toluene, and xylene.

Table 1

Solvent	Molecular extinction coefficient
Ethyl acetate + Buthyl alcohol (4 : 1)	31722
Ethyl acetate	28483
Ethyl acetate + Amyl alcohol (4 : 1)	25467
Amyl acetate	20441
Buthyl acetate	20441
Iso-buthyl alcohol	16755
Chloroform	16364
Iso-amyl alcohol	13627

Table 2

Amount of iron (γ)	Absorbance		
	1st extract	2nd extract	3rd extract
5	0.505	0.006	0.005

5. Concentration of the acid

The optimum concentration of the acid for extraction ranged from 1N acidity to pH 2.5, as shown in Fig. 4. The absorbance decreased slowly above pH 2.5, and rapidly at pH 4.7, and then the extraction became almost impossible. At a stronger acidity than pH 1.8, a precipitate of antipyrine and potassium thiocyanate was formed but dissolved when ethyl acetate was added. The extraction could be made quantitatively up to the acid concentration of 1N, but the absorbance decreased at 1.2N, and further decreased with the increase in the acidity as shown in Fig. 4. The acid used might be hydro-

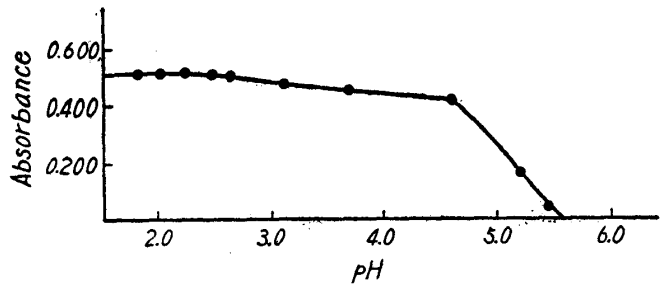

Fig. 4. Effect of hydrogen ion concentration on the absorbance of iron-antipyrine-thiocyanate complex.

chloric, sulfuric, or nitric acid.

6. Amount of antipyrine and potassium thiocyanate

Using 5 γ of iron, 5 ml of 0.1N hydrochloric acid, and 5 ml of 5 per cent antipyrine solution, extraction was made with 5 ml of ethyl acetate and with various amounts of potassium thiocyanate. It was found that over 3 ml of 20 per cent potassium thiocyanate solution was necessary. Similarly, by using 5 ml of 20 per cent potassium thiocyanate solution, it was found that 2 ml of 5 per cent antipyrine solution was sufficient for the present purpose.

7. Relation between the amount of the iron and absorbance

As shown in Fig. 5, there is a linear relation between the amount of iron and the absorbance, obtained from 5 ml of 0.1N hydrochloric acid, 5 ml of 20 per cent potassium thiocyanate solution, and 5 ml of 5 per cent antipyrine solution, with various amounts of iron and extracting with 5 ml of ethyl acetate, measured at 470 mμ. It was seen that Beer's law was obeyed and the determination was possible within a range of 0.2~10 γ of iron.

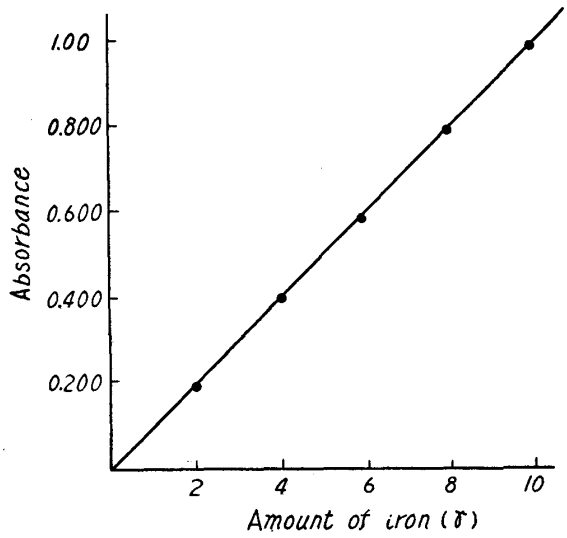

Fig. 5. Calibration curve of iron.

8. Effect of divers ions

In the determination of iron, interferences by elements which were likely to be present were studied and it was seen that manganese, magnesium, calcium, aluminum, trivalent arsenic, chromium, nickel, lead, zinc, cadmium, mercury, and tin had no effect, while copper, bismuth, and cobalt interfered in it.

Summary

(1) Iron forms a red compound with antipyrine and potassium thiocyanate, and this compound can be extracted with an organic solvent. A minute amount of iron below 1 γ can be determined by measuring the absorbance of this extract at the optimum wave length of 470 mμ.

(2) Ethyl acetate is the best extraction solvent, while a mixed solvent of the acetate and isobutyl alcohol (4 : 1) gives a slightly larger molecular extinction coefficient.

(3) The concentration of the acid suited for the extraction ranges from 1N acidity to pH 2.5.

(4) The chief interfering elements are copper, bismuth, and cobalt.

Acknowledgement

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